

Identification of mixite minerals – an SEM and Raman spectroscopic analysis

Ray L. Frost*, Matt Weier, Wayde Martens and Loc Duong

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Frost, Ray and Weier, Matt and Martens, Wayde and Duong, Loc (2005) Identification of mixite minerals – an SEM and Raman spectroscopic analysis. *Mineralogical Magazine* 69(2):169-177.

Abstract:

Two mixites from Boss Tweed Mine, Tintic District, Juab Vounty, Utah and Tin Stope, Majuba Hill, Pershing Co., Nevada have been analysed by SEM with EDX analysis and by Raman spectroscopy. The SEM images show the mixite crystals to be elongated fibres up to 200 μm in length and 2 μm in width. Detailed images of the mixite crystals show the mineral to be composed of bundles of fibres. The EDX analyses depend on the crystal studied, however the Majuba mixite gave analyses which matched the formula $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$. Raman bands observed in the region 880 to 910 cm^{-1} and in the 867 to 870 cm^{-1} region are assigned to the AsO stretching vibrations of $(\text{HAsO}_4)^{2-}$ and $(\text{H}_2\text{AsO}_4)^-$ units. Whilst bands at 803 and 833 cm^{-1} are assigned to the stretching vibrations of uncomplexed $(\text{AsO}_4)^{3-}$ units. Intense bands are observed at 473.7 and 475.4 cm^{-1} are assigned to the ν_4 bending mode of AsO_4 units. Bands observed at 386.5, 395.3 and 423.1 cm^{-1} are assigned to the ν_2 bending modes of the HAsO_4 (434 and 400 cm^{-1}) and the AsO_4 groups (324 cm^{-1}). Raman spectroscopy lends itself to the identification of minerals on host matrices and is especially useful for the identification of mixites.

Key words- agardite, analytical detection, mixite, petersite, identification, Raman spectroscopy, SEM

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)

Introduction

Mixite is the mineral of formula $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ and is related to agardites. Mixites are secondary minerals associated with Bi bearing ores. The minerals are white or yellow-green through to blue green and are acicular or needle like crystal formation. The minerals are often found with bismutite ($\text{Bi}_2(\text{CO}_3)_2\text{O}_2$), atelestite ($\text{BiO}(\text{OH})(\text{AsO}_4)$), erythrite ($\text{Co}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) and barite (BaSO_4). Agardite is a member of the mixite group, $\text{ACu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ for the fully hydrated formula, with (A = lanthanide³⁺). Mixite (A = Bi), goudeyite (A = Al), zalesiite (A = Ca, with protonation of the lattice for charge compensation) and petersite-(Y), the phosphate analogue of agardite-(Y) are recognized isomorphous species in the group. Of the many possible rare earth congeners constituting the agardite group, only agardite-(Y) and agardite-(La) are recognized as distinct species by the IMA. (Anthony *et al.*, 2003) Others have been reported in the literature (Walenta, 1960; Dunin-Barkovskaya, 1976; Hess, 1983; Olmi *et al.*, 1988; Braithwaite and Knight, 1990; Krause *et al.*, 1997) but their species status remains unresolved. It should be noted that formulae given above refer to ideal, end-member compositions; extensive solid solution involving P for As substitution is known for naturally occurring material. Water in the lattice is for the most part thought to be zeolitic in nature, as evidenced by single-crystal X-ray structure determinations (Bayliss *et al.*, 1966; Aruga and Nakai, 1985; Miletich *et al.*, 1997). The crystal structures of natural mixite and agardite compounds reveal a microporous framework structure (Hess, 1983; Aruga and Nakai, 1985) with a framework similar to that of zeolites (Miletich *et al.*, 1997) Dietrich *et al.* (Dietrich *et al.*, 1969). originally proposed that the water in agardite was zeolitic. As such these minerals may have potential for catalytic applications.

The mixite group consists of secondary minerals formed through crystallisation from aqueous solution. The conditions under which this crystallisation takes place, particularly relating to anion and cation concentrations, pH, temperature and kinetics of crystallisation, determines the particular mineral that is formed. Recently, Raman spectroscopy has been used to gain an understanding of many

properties of secondary minerals (Frost, 2003; Frost *et al.*, 2003a; Frost *et al.*, 2003b; Frost and Klopogge, 2003; Frost *et al.*, 2003c; Martens *et al.*, 2003a; Martens *et al.*, 2003b). In this research we report the analysis of two mixite minerals by SEM, EDX and Raman spectroscopy.

Minerals

The mixite minerals used in this work were obtained from (a) Museum Victoria (b) Mineral research Company and the author's personal collection. Two mixites were selected for study from a large collection of mixite mineral samples: these are mixite from Boss Tweed Mine, Tintic District, Juab Vounty, Utah and a mixite from Tin Stope, Majuba Hill, Pershing Co., Nevada.

SEM and X-ray microanalysis

Mixite samples were coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at 25kV accelerating voltage. Preliminary analyses of the mixite samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system.

Raman microprobe spectroscopy

The crystals of the mixites were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a thermo-electrically

cooled Charge Coupled Device (CCD) detector. Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. The crystals were oriented to provide maximum intensity. All crystal orientations were used to obtain the spectra. Power at the sample was measured as 1 mW.

The Galactic software package GRAMS was used for data analysis. Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of R^2 greater than 0.995.

RESULTS AND DISCUSSION

Mixite is the mineral of formula $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ (Walenta, 1960; Mereiter and Preisinger, 1986). Five different vibrating units will contribute to the overall spectral profile, namely the OH units, the water molecules, AsO_4 groups, the HAsO_4 groups and the coordination polyhedra of the Bi and Cu. The first two vibrating species will contribute to the high wavenumber region whilst the AsO_4 units will show Raman bands below 1200 cm^{-1} . (Ross, 1972) It has been shown that the water can be reversibly lost and the number of water molecules per formula unit can vary up to 3. According to Mereiter and Preisinger (1986) mixites have a microporous framework structure based upon $(\text{M}^{3+})_{1-x}(\text{M}^{2+})_x\text{Cu}_6(\text{OH})_6(\text{AsO}_4)_{3-x}(\text{AsO}_3\text{OH})_x$. (Mereiter and Preisinger, 1986), with vacancies in the A site or substitution by divalent cations being compensated by protonation of the lattice.

SEM analyses

The EDX analyses for the mixites from Majuba Hill slope and Boss tweed mine are shown in Figures 1a and 1b respectively. The results of the EDX analyses are reported in Table 1. The analyses of the other two minerals (Conichalcite Central Pit, Gold Hill, Tooele County, Utah, USA. Mammoth Mine, Tintic District, Utah, USA) were undertaken but little to no As or P was found. Hence the minerals were not mixites. The analyses of the Boss sample showed high Cu and As and low Bi as well as low O. The two Boss samples analysed the same. The two Majuba samples marked Majuba 2 and 3 analysed the same and the results are very close to the theoretical values.

SEM images

The SEM images of the two mixites (Boss and Majuba) are shown in Figures 2a and b. A detailed image of the Majuba mixite fibres are shown in Figure 2c. The most striking feature of the SEM images is the fibre like nature of the mixite minerals. The fibres of the Boss mixite are long with lengths exceeding 50 μm with widths 1 to 2 μm . The Majuba mixite also shows the fibrous nature of the mixite crystals. Some of the fibres are 200 μm in length. The Majuba mixite crystals seem to be made up of bundles of fibres.

Raman spectroscopy

On the spectroscopic time scale, exchange of protons between water molecules and arsenate ions is also likely. According to this formulation two types of units involving As are found, namely AsO_4 and HAsO_4 . Thus two sets of bands involving AsO stretching modes would be expected. Vibrational spectroscopy has been used to study the coordination chemistry of $(\text{AsO}_4)^{3-}$ ions for some considerable time. (Siebert, 1954; Ross, 1972; Vansant and Van der Veken, 1973; Vansant *et al.*, 1973; Myneni *et al.*, 1998b; Myneni *et al.*, 1998a) Vansant *et al.* showed the frequencies of the $(\text{AsO}_4)^{3-}$ units of Td symmetry as 818 (A_1), 786 (F-stretching), 405 (F-bending) and 350 cm^{-1} (E). (Vansant *et al.*, 1973) Vibrational spectroscopic studies have shown that the symmetry of the $(\text{AsO}_4)^{3-}$ polyhedron are strongly distorted and the $(\text{AsO}_4)^{3-}$ vibrations are strongly influenced by the protonation, cation presence and water coordination. (Vansant and Van der Veken, 1973; Vansant

et al., 1973; Myneni et al., 1998b; Myneni et al., 1998a) The symmetric stretching vibration of the arsenate anion in aqueous systems (ν_1) is observed at 810 cm^{-1} and coincides with the position of the antisymmetric stretching mode (ν_3). (Ross, 1972) The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the (ν_4) bending modes at 398 cm^{-1} . Of all the tetrahedral oxyanions, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions.

The Raman spectra of the selected mixites in the 200 to 3800 cm^{-1} region (the full spectrum), 700 to 1100 cm^{-1} region, 200 to 600 cm^{-1} region, 3000 to 3800 cm^{-1} region at 298 are shown in Figures 3, 4, 5 and 6 respectively. The results of the Raman spectral analysis are reported in Table 2. Figure 3 displays the spectra for the $(\text{AsO}_4)^{3-}$ and $(\text{HAsO}_4)^{2-}$ stretching region. Clearly the 298 K spectra from the Boss Tweed mine and the Majuba Hill mine show peaks in the 850 to 830 cm^{-1} region which are indicative $(\text{AsO}_4)^{3-}$ bands. Two Raman bands may be observed in the region 880 to 910 cm^{-1} and in the 867 to 870 cm^{-1} region. These are assigned to the AsO stretching vibrations of $(\text{HAsO}_4)^{2-}$ and $(\text{H}_2\text{AsO}_4)^-$ units (Vansant and Van der Veken, 1973; Vansant et al., 1973). The Raman spectrum of the Boss mineral in the 700 to 1100 cm^{-1} region shows three bands at 851.8 , 830.8 and 808 cm^{-1} . The Majuba mineral Raman spectrum shows $(\text{AsO}_4)^{3-}$ stretching bands at 854.3 , 831.5 and 809.8 cm^{-1} . The band positions are slightly higher for the Majuba sample compared with that of the Boss sample. This is a result of the different chemical compositions of the two mixites (refer Table 1). The principal difference in the chemical composition appears to be the additional Ca in the Boss sample. The Ca is substituting for the Cu in the mixite mineral. The value for Ca for the Boss sample is 0.13 and for the Majuba mixite is 0.08 . According to Myeni et al. (see Myeni table 3) the band at 915 cm^{-1} corresponds to the antisymmetric stretching vibration of protonated $(\text{AsO}_4)^{3-}$ units and the band at 880 cm^{-1} to the symmetric stretching vibration of the protonated $(\text{AsO}_4)^{3-}$ units (Myneni et al., 1998b; Myneni et al., 1998a). The position of the bands indicate a C_{2v} symmetry of the $(\text{HAsO}_4)^{2-}$ anion. For the two mixites no band was observed in the 867 to 870 cm^{-1} region. This suggests there are no $(\text{H}_2\text{AsO}_4)^-$ units in the sample. For the Boss sample two bands are observed at 880.6 and 851.8 cm^{-1} with band widths of 30.1 and 35.9 cm^{-1} . These bands shift to 878.8 and 910.4

cm^{-1} at 77 K with band widths of 36.3 and 24.9 cm^{-1} . For the Majuba sample only a single band was found at 909.7 cm^{-1} in the 298 K spectrum. Two bands are found at 803 and 833 cm^{-1} . These are assigned to the stretching vibrations of uncomplexed $(\text{AsO}_4)^{3-}$ units. The bands correspond to the antisymmetric (803 cm^{-1}) and symmetric (833 cm^{-1}) stretching vibrations of $(\text{AsO}_4)^{3-}$ units of T_d symmetry (Myneni et al., 1998b; Myneni et al., 1998a). In the case of the Boss mineral, the first band is found at 805.1 cm^{-1} and for the Majuba mineral at 809.8 cm^{-1} . The bands shift to 806.6 and 809.2 cm^{-1} in the 77 K spectrum. Two bands are found at 830.8 cm^{-1} and 851.8 cm^{-1} for the Boss mineral and at 831.5 and 854.3 cm^{-1} for the Majuba mineral.

A number of bands are observed in the 350 to 550 cm^{-1} region (Figure 4). A band is observed at 539 cm^{-1} which is cation sensitive. One possible assignment is that the band is the ν_4 bending mode of $(\text{HAsO}_4)^-$ units. Such a band position was not observed in the work of Vansant et al. (Vansant and Van der Veken, 1973; Vansant et al., 1973) and was not reported as was any of the bending modes in the work of Myeni et al. (Myneni et al., 1998b; Myneni et al., 1998a). Theoretical studies have shown such bond distances are dependent upon the type of arsenate unit in the structure (Myneni et al., 1998b; Myneni et al., 1998a) (see for example Table 2 in the Myeni reference). Such bond distances are cation sensitive for example the As-O bond distance is 1.62 Å for $\text{Al-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$, 1.65 Å for $\text{Mg-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$, 1.66 Å for $\text{CdO}_2\text{-AsO}_2(\text{H}_2\text{O})_4$ and 1.64 Å for $\text{Cd-O}_2\text{-AsO}_2(\text{H}_2\text{O})_4$. Such cationic sensitivity is expected to be translated to the bending modes of the $(\text{HAsO}_4)^-$ units. Vansant et al showed the potential energy distributions for $(\text{AsO}_4)^{3-}$, $(\text{HAsO}_4)^{2-}$ and $(\text{H}_2\text{AsO}_4)^-$ units (Vansant and Van der Veken, 1973). These distributions were then used to calculate the attribution of the vibrational modes (Vansant and Van der Veken, 1973).

Intense bands are observed at 473.7 and 475.4 cm^{-1} (Boss), 475.1 (Majuba) and are assigned to the ν_4 antisymmetric bending mode of AsO_4 units. An additional band is observed 458.4 cm^{-1} (Boss); 459.5 (Majuba). Three bands are observed at 386.5, 395.3 and 423.1 cm^{-1} and are of similar intensities. These are assigned to the ν_2 bending modes of the HAsO_4 (423.1 and 395.3 cm^{-1}) and the AsO_4 groups (386.5 cm^{-1}). For the Majuba sample two bands are observed at 393.2 and 422.7 cm^{-1} . These bands shift to 394.4 and 424.0 cm^{-1} at 77 K. The spectral pattern in the 350 to

550 cm^{-1} region is very similar for the Boss and Majuba samples and appears to be characteristic of the Raman spectrum of the mixite minerals.

The Raman spectra of the OH stretching region are shown in Figure 5. For a mixite of formula $\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ there should be two types of OH units: firstly one from the OH units and the second from the interlamellar water. A band is observed at 3473.9 cm^{-1} (Boss) and 3470.3 cm^{-1} (Majuba) with bandwidths of 37.5 cm^{-1} and 34.2 cm^{-1} . This band is attributed to the OH stretching vibration of the hydroxyl units. A second band is observed at 3428.4 cm^{-1} (Boss) and 3444.0 cm^{-1} (Majuba) and may also be assigned to OH stretching vibrations. This suggests two non-equivalent OH units in the mixite crystal structure. An intense broad band is found at 3386.7 cm^{-1} (298 K) and at 3394.2 cm^{-1} (77 K) for Boss mineral and at 3412.3 cm^{-1} (298 K) and 3402.7 cm^{-1} (77 K) for the Majuba sample. These bands are assigned to the interlamellar water in the mixite structure.

Studies have shown a strong correlation between OH stretching frequencies and both O...O bond distances and H...O hydrogen bond distances (Novak, 1974; Emsley, 1980; Mikenda, 1986; Lutz, 1995). Libowitzky based upon the hydroxyl stretching frequencies as determined by infrared spectroscopy, showed that a regression function can be employed relating the above correlations with regression coefficients better than 0.96 (Libowitzky, 1999). The function is $\nu_1 = 3592 - 304 \times 10^9 \exp(-d(\text{O}-\text{O})/0.1321) \text{ cm}^{-1}$. If the assumption is made that the wavenumber of the Raman OH stretching vibrations can be used instead of the infrared band, then estimations of the hydrogen bond distances can be made. The H-bond distance for the OH units are 2.819 Å (3428.4 cm^{-1}) and 2.862 Å (3473.9 cm^{-1}) and the H-bond distances of the water are 2.784 (3377.6 cm^{-1}) and 2.789 Å (3386.7 cm^{-1}). There are two distinct hydrogen bond distances namely 2.78 Å and 2.86 Å. The water is more strongly hydrogen bonded than the OH units. The water is hydrogen bonded to other water molecules and may also coordinate the AsO_4 units atom.

CONCLUSIONS

Mixites are an uncommon secondary mineral found in the oxidised zone of copper deposits. The minerals contain bismuth and are often mixed with other

bismuth based minerals such as malachite, bismuthite and atelestite. EDX analyses have been used to determine the chemical composition of the two mixites. SEM analyses show the minerals to have elongated crystals of a fibrous nature up to 200 μm long. The minerals show the characteristic Raman spectra of arsenate containing minerals.

Acknowledgments

The financial and infrastructure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged.

The Australian Research Council (ARC) is thanked for funding.

References

- Anthony, J.W., Bideaux, R.A., Bladh, K.W., and Nichols, M.C. (2003) Handbook of mineralogy Vol.V. Borates, Carbonates, Sulphates. - Mineral Data Publishing, Tucson, Arizona. *Handbook of mineralogy Vol.V. Borates, Carbonates, Sulphates. - Mineral Data Publishing, Tucson, Arizona.*
- Aruga, A., and Nakai, I. (1985) Structure of calcium-rich agardite, $(\text{Ca}_{0.40}\text{Y}_{0.31}\text{Fe}_{0.09}\text{Ce}_{0.06}\text{La}_{0.04}\text{Nd}_{0.01})\text{Cu}_{6.19}[(\text{AsO}_4)_{2.42}(\text{HAsO}_4)_{0.49}](\text{OH})_{6.38}\cdot 3\text{H}_2\text{O}$. *Acta Crystallographica, Section C: Crystal Structure Communications*, **C41**(2), 161-3.
- Bayliss, P., Lawrence, L.J., and Watson, D. (1966) Rare copper arsenates from Dome Rock, South Australia. *Australian Journal of Science*, **29**(5), 145-6.
- Braithwaite, R.S.W., and Knight, J.R. (1990) Rare minerals, including several new to Britain, in supergene alteration of uranium-copper-arsenic-bismuth-cobalt mineralization near Dalbeattie, south Scotland. *Mineralogical Magazine*, **54**(374), 129-31.
- Dietrich, J.E., Orliac, M., and Permingeat, F. (1969) Agardite, a new mineral species and the chlorotile problem. *Bulletin de la Societe Francaise de Mineralogie et de Cristallographie*, **92**(5), 420-34.

- Dunin-Barkovskaya, E.A. (1976) Arsenates. Hydrous arsenates. Mixite $(\text{Cu}_{12}\text{Bi}[(\text{AsO}_4)_6(\text{OH})_9] \cdot 9\text{H}_2\text{O})$. *Miner. Uzb.*, **3**, 25-6.
- Emsley, J. (1980) Very strong hydrogen bonding. *Chemical Society Reviews*, **9**, 91-124.
- Frost, R.L. (2003) Raman spectroscopy of selected copper minerals of significance in corrosion. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, **59A**(6), 1195-1204.
- Frost, R.L., Crane, M., Williams, P.A., and Klopogge, J.T. (2003a) Isomorphic substitution in vanadinite $[\text{Pb}_5(\text{VO}_4)_3\text{Cl}]$ -a Raman spectroscopic study. *Journal of Raman Spectroscopy*, **34**(3), 214-220.
- Frost, R.L., Duong, L., and Martens, W. (2003b) Molecular assembly in secondary minerals - Raman spectroscopy of the arthurite group species arthurite and whitmoreite. *Neues Jahrbuch fuer Mineralogie, Monatshefte*(5), 223-240.
- Frost, R.L., and Klopogge, J.T. (2003) Raman spectroscopy of some complex arsenate minerals-implications for soil remediation. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, **59A**(12), 2797-2804.
- Frost, R.L., Williams, P.A., Klopogge, J.T., and Martens, W. (2003c) Raman spectroscopy of the copper chloride minerals nantokite, eriochalcite and claringbullite - implications for copper corrosion. *Neues Jahrbuch fuer Mineralogie, Monatshefte*(10), 433-445.
- Hess, H. (1983) The crystal structure of chlorotile, $\text{SECu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ (SE = rare earth metals). *Neues Jahrbuch fuer Mineralogie, Monatshefte*(9), 385-92.
- Krause, W., Bernhardt, H.J., Blass, G., Effenberger, H., and Graf, H.W. (1997) Hechtsbergite, $\text{Bi}_2\text{O}(\text{OH})(\text{VO}_4)$, a new mineral from the Black Forest, Germany. *Neues Jahrbuch fuer Mineralogie, Monatshefte*(6), 271-287.
- Libowitzky, E. (1999) Correlation of the O-H stretching frequencies and the O-H...H hydrogen bond lengths in minerals. *Monatshefte für chemie*, **130**, 1047-1049.
- Lutz, H. (1995) Hydroxide ions in condensed materials - correlation of spectroscopic and structural data. *Structure and Bonding (Berlin, Germany)*, **82**, 85-103.
- Martens, W., Frost, R.L., Klopogge, J.T., and Williams, P.A. (2003a) Raman spectroscopic study of the basic copper sulphates-implications for copper corrosion and \"bronze disease\". *Journal of Raman Spectroscopy*, **34**(2), 145-151.

- Martens, W.N., Frost, R.L., and Williams, P.A. (2003b) The basic copper phosphate minerals pseudomalachite, ludjibaite and reichenbachite: An infrared emission and Raman spectroscopic study. *Neues Jahrbuch fuer Mineralogie, Monatshefte*(8), 337-362.
- Mereiter, K., and Preisinger, A. (1986) Kristallstrukturdaten der wismutminerale atelestit, mixit und pucherit. *Anzeiger der Osterreichischen Akademie der Wissenschaften, math.-natuwiss. Klasse*, **123**, 79-81.
- Mikenda, W. (1986) Stretching frequency versus bond distance correlation of O-D(H)...Y (Y = N, O, S, Se, Cl, Br, I) hydrogen bonds in solid hydrates. *Journal of Molecular Structure*, **147**, 1-15.
- Miletich, R., Zemann, J., and Nowak, M. (1997) Reversible hydration in synthetic mixite, $\text{BiCu}_6(\text{OH})_6(\text{AsO}_4)_3 \cdot n\text{H}_2\text{O}$ ($n \approx 3$): hydration kinetics and crystal chemistry. *Physics and Chemistry of Minerals*, **24**(6), 411-422.
- Myneni, S.C.B., Traina, S.J., Waychunas, G.A., and Logan, T.J. (1998a) Experimental and theoretical vibrational spectroscopic evaluation of arsenate coordination in aqueous solutions, solids, and at mineral-water interfaces. *Geochimica et Cosmochimica Acta*, **62**(19/20), 3285-3300.
- . (1998b) Vibrational spectroscopy of functional group chemistry and arsenate coordination in ettringite. *Geochimica et Cosmochimica Acta*, **62**(21/22), 3499-3514.
- Novak, A. (1974) Hydrogen bonding in solids. Correlation of spectroscopic and crystallographic data. *Structure and Bonding (Berlin)*, **18**, 177-216.
- Olmi, F., Sabelli, C., and Brizzi, G. (1988) Agardite-(Y), gysinite-(Nd) and other rare minerals from Sardinia. *Mineralogical Record*, **19**(5), 305-10.
- Ross, S.D. (1972) Inorganic Infrared and Raman Spectra (European Chemistry Series). 414 pp. p.
- Siebert, H. (1954) Force constants and chemical structure. V. The structure of oxygen acids. *Z. anorg. u. allgem. Chem.*, **275**, 225-40.
- Vansant, F.K., and Van der Veken, B.J. (1973) Vibrational analysis of arsenic acid and its anions. II. Normal coordinate analysis. *Journal of Molecular Structure*, **15**(3), 439-44.
- Vansant, F.K., Van der Veken, B.J., and Desseyn, H.O. (1973) Vibrational analysis of arsenic acid and its anions. I. Description of the Raman spectra. *Journal of Molecular Structure*, **15**(3), 425-37.

Walenta, K. (1960) Chlorotile and mixite. *Neues Jahrbuch fuer Mineralogie, Monatshefte*, 223-36.

List of Figures

Figure 1a EDX analysis of the Majuba mixite

Figure 1b EDX analysis of the Boss mixite

Figure 2a SEM image of the Boss mixite

Figure 2b SEM image of the Majuba mixite

Figure 3 Raman spectra of selected mixites at 298 K.

Figure 4 Raman spectra of selected mixites in the 700 to 1100 cm^{-1} region at 298 K.

Figure 5 Raman spectra of selected mixites in the 200 to 600 cm^{-1} region at 298 K.

Figure 6 Raman spectra of selected mixites in the 3000 to 3800 cm^{-1} region at 298 K.

List of Tables

Table 1 Results of the EDX analyses of the Boss and Majuba mixites

Table 2 Results of the Raman spectra of the mixites from Boss and Majuba

Table 1 Results of the EDX analyses of the Boss and Majuba mixites

$\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ N=31

Bi = 3.23%
 Cu = 19.35%
 As = 9.68%
 O = 67.74%

 100%

Analyses

	Theory	Boss1	Boss2	Majuba1	Majuba2	Majuba3
O	67.74	43.94	46.74	38.39	62.33	65.12
Cu	19.35	32.56	31.60	36.51	17.86	17.70
As	9.68	16.18	15.46	17.11	9.39	9.19
Bi	3.23	3.75	3.73	4.35	2.48	2.50
Si	-	0.97	0.28	0.66	2.40	0.82
Ca	-	2.26	1.91	1.30	0.61	0.72
Fe	-	0.35	0.27	0.19	0.53	0.37
Al	-	-	-	1.49	4.41	3.57

Calculations

$\text{Bi}_{1/3}\text{Cu}_2\text{As}_1\text{O}_7\text{H}_4$

	Theory	Boss1	Boss2	Majuba1	Majuba2	Majuba3
O	7.00	2.72	3.02	2.24	6.64	7.09
Cu	2.00	2.01	2.04	2.13	1.90	1.93
As	1.00	1.00	1.00	1.00	1.00	1.00
Bi	0.33	0.23	0.24	0.25	0.26	0.27
Si		0.06	0.02	0.04	0.26	0.09
Ca		0.14	0.12	0.08	0.06	0.08
Fe		0.02	0.02	0.01	0.06	0.04
Al				0.09	0.47	0.39

Elemental ratios for mixite normalised against As, formula and sample values.

Table 2 Results of the Raman spectra of the mixites from Boss and Majuba

Boss			Majuba		
Center	FWHM*	%**	Center	FWHM	%
3473.9	37.5	1.4	3470.3	34.2	1.1
			3444.0	65.2	0.7
3428.4	45.3	1.5	3412.3	213.0	9.2
3386.7	233.2	16.9			
3377.6	80.9	3.8			
1044.1	22.0	0.3	1055.0	69.0	0.4
1014.7	4.5	0.1			
988.2	47.6	2.5	986.0	63.0	2.9
909.9	35.9	1.1	909.7	29.5	1.1
880.6	30.1	2.0	864.6	60.3	11.9
851.8	18.8	22.2	854.3	19.9	37.4
830.8	25.3	9.6	831.5	17.2	1.3
808.0	19.3	4.2	809.8	24.4	8.1
805.1	61.7	3.7			
717.4	94.2	1.1	707.6	55.1	0.4
			565.3	19.4	0.2
547.2	36.8	1.2			
531.0	13.5	0.4	530.5	13.7	0.3
			522.7	61.0	3.4
			490.3	28.3	2.2
475.4	14.9	6.7	475.1	18.6	6.3
473.7	62.6	8.7			
458.4	10.3	0.3	459.5	39.2	3.4
432.5	13.2	0.4			
423.1	16.9	3.6	422.7	20.0	2.7
395.3	14.0	1.8	393.2	22.1	1.5
386.5	24.9	1.9			
334.3	15.6	0.3			
319.5	16.6	1.3	314.4	27.7	1.7
302.5	7.3	0.1			
282.5	14.5	0.4	285.9	27.6	1.0
249.0	10.7	0.1	250.9	15.1	0.6
			241.8	48.4	1.0
227.8	23.8	1.0	229.9	19.7	0.6
192.0	19.8	0.9	198.9	18.2	0.4
178.4	9.5	0.2	178.1	9.5	0.1
158.9	5.1	0.0			

*FWHM=full width of the band at half the maximum intensity.

** % = Relative intensity.

Label A: Mixite Majuba single crystal

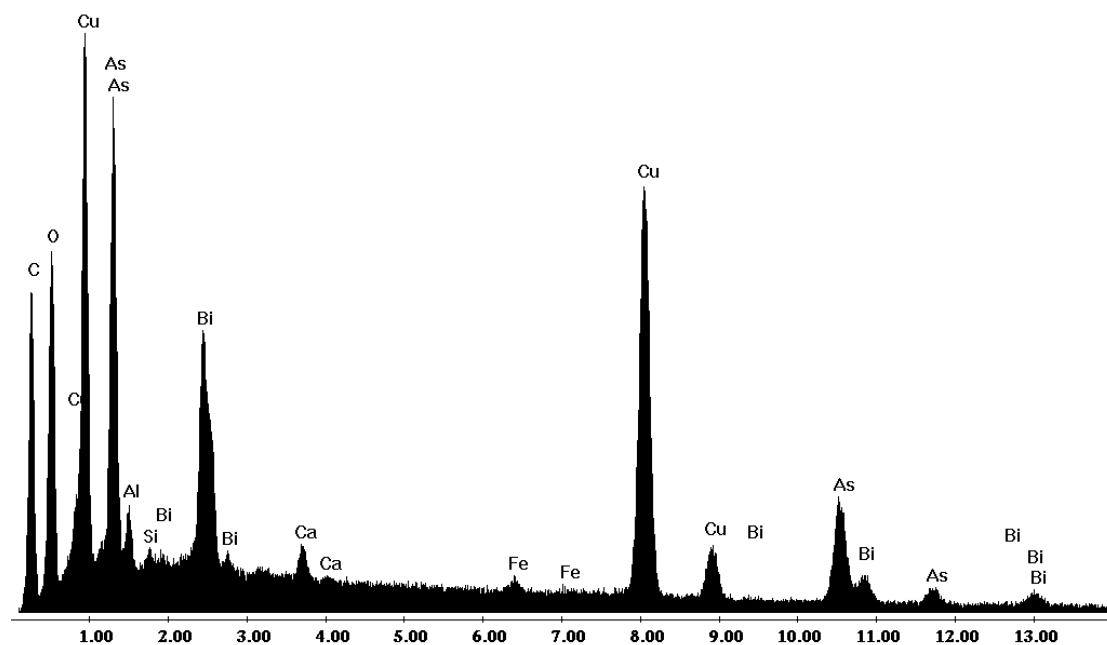


Figure 1a EDX analysis of Majuba Mixite

Label A: Mixite Boss

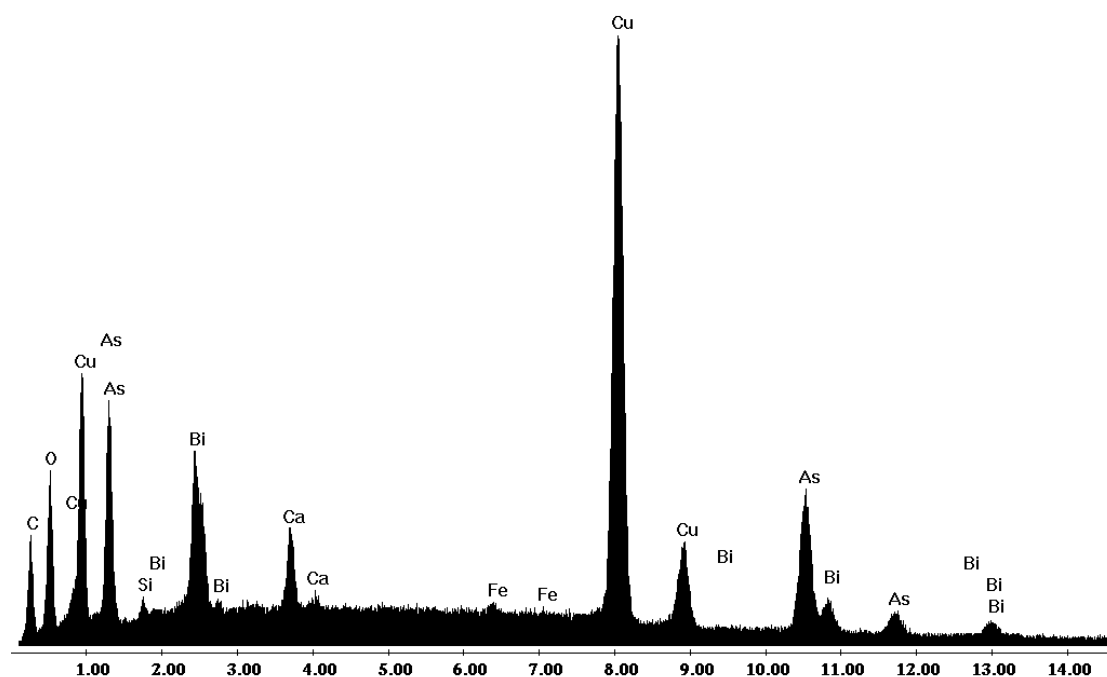


Figure 1b EDX analysis of Boss Mixite

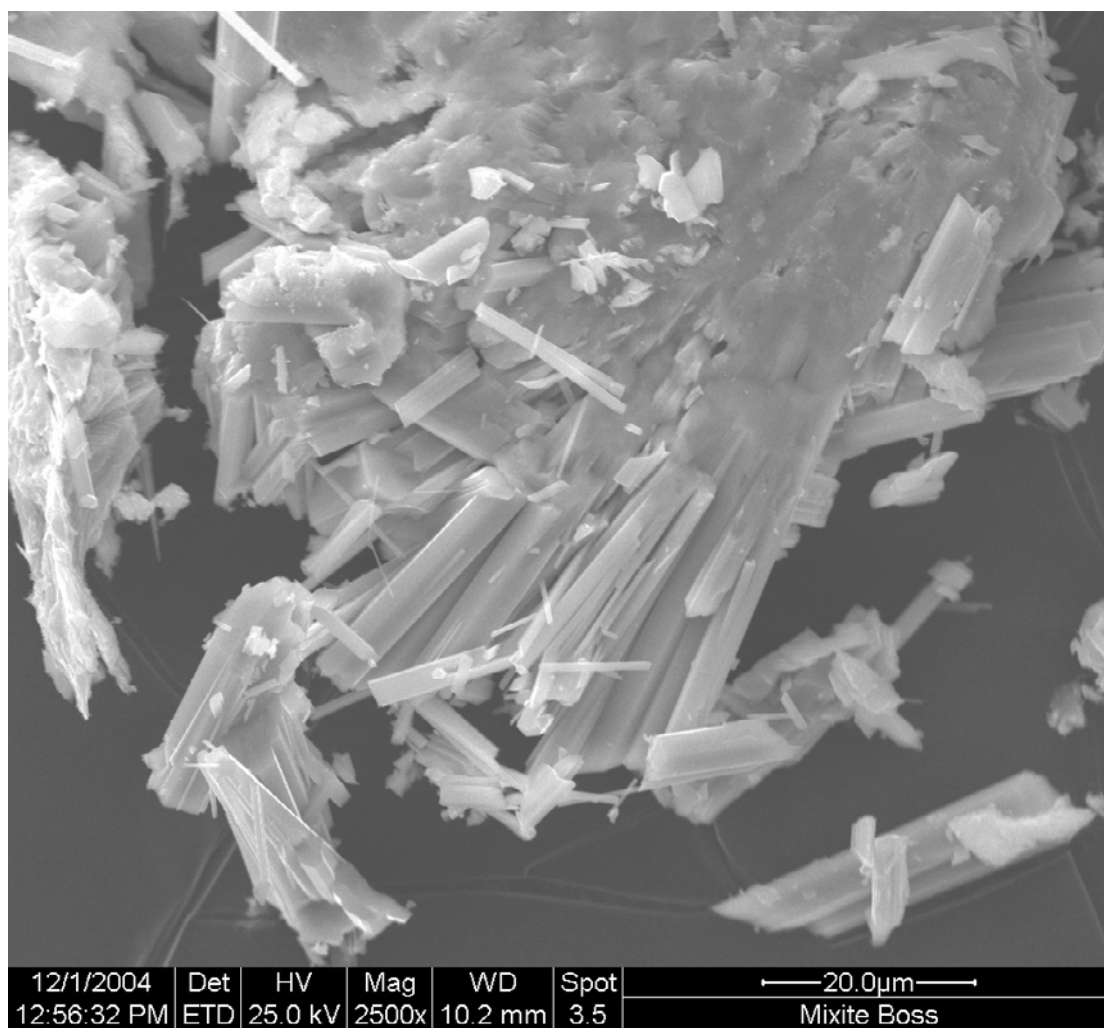


Figure 2a SEM image of the Boss mixite

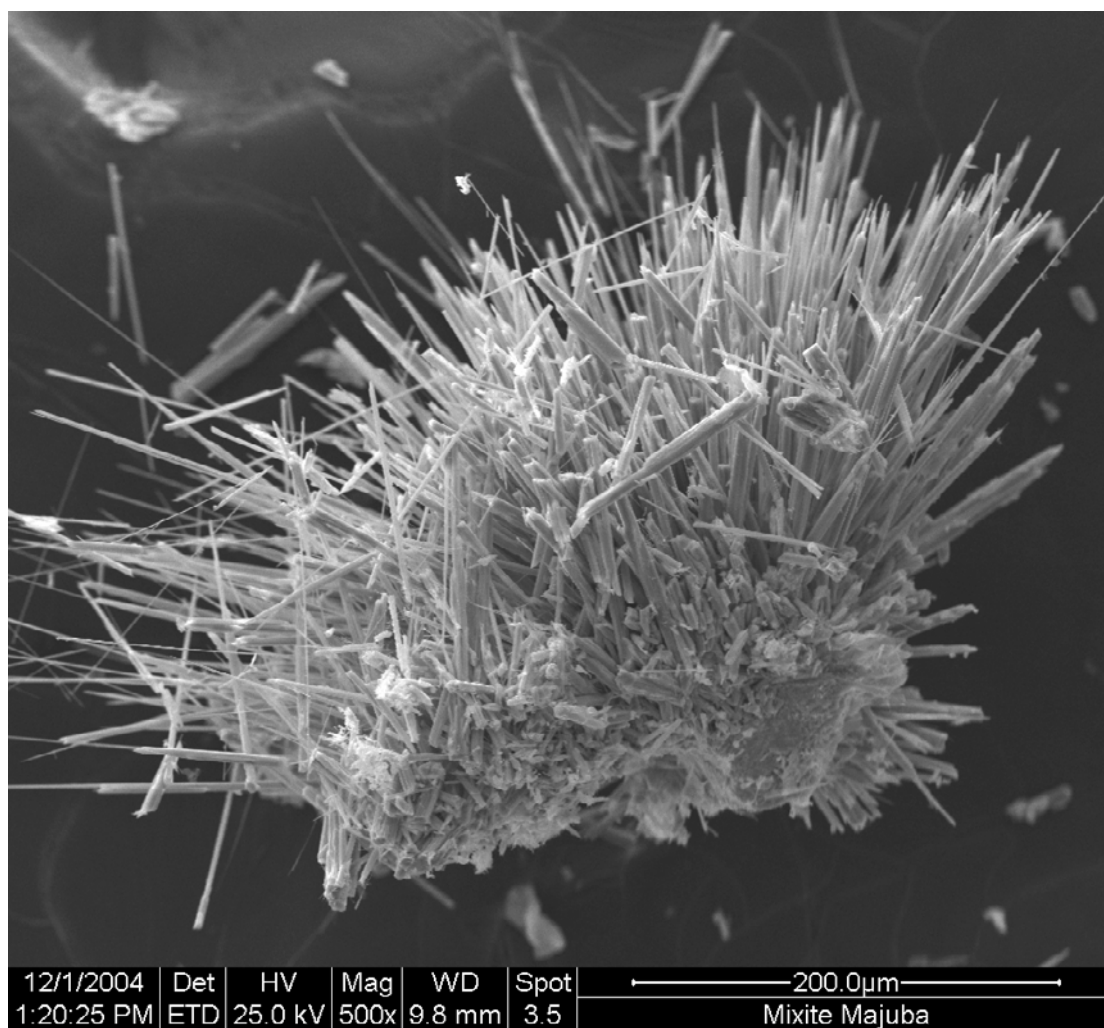


Figure 2b SEM image of Majuba mixite

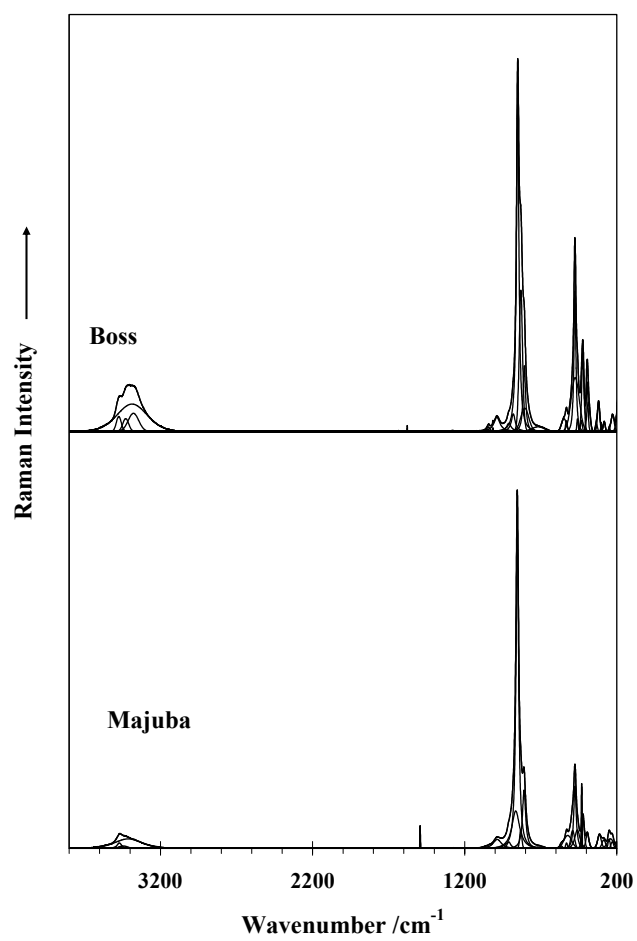


Figure 3

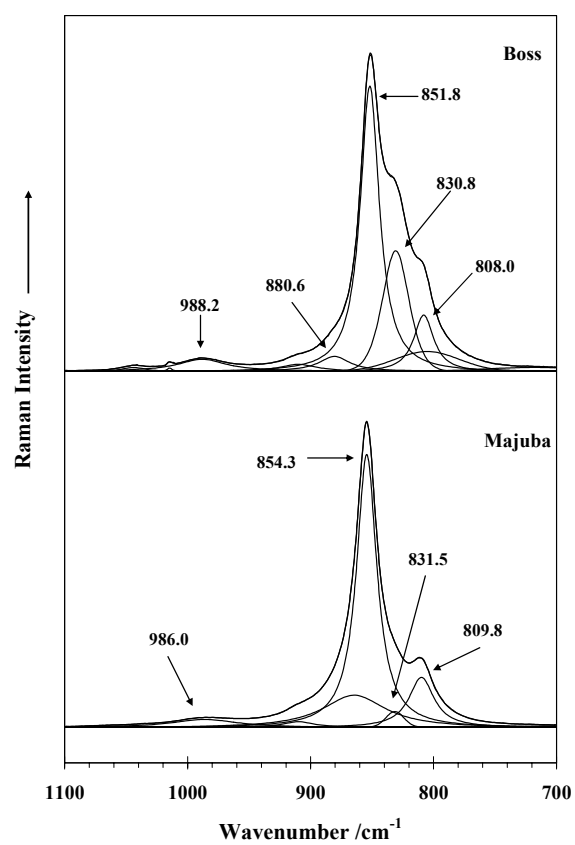


Figure 4

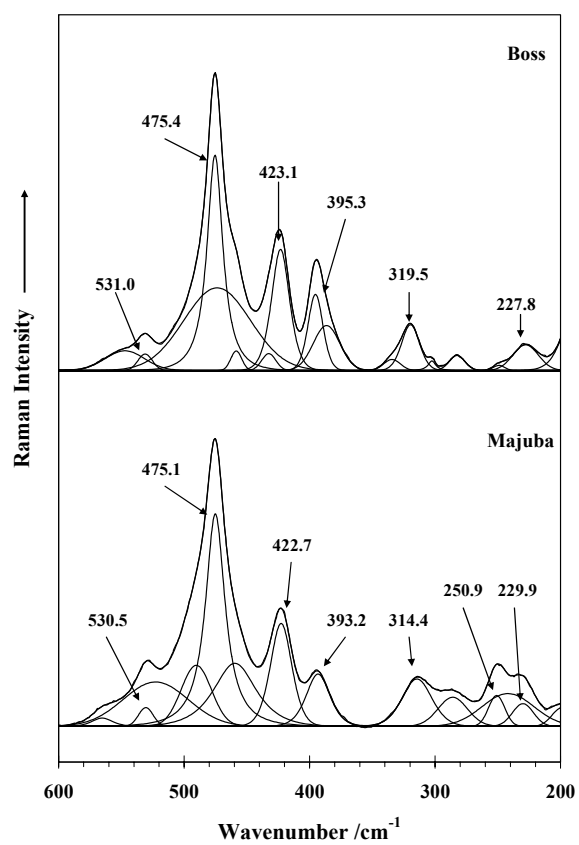


Figure 5

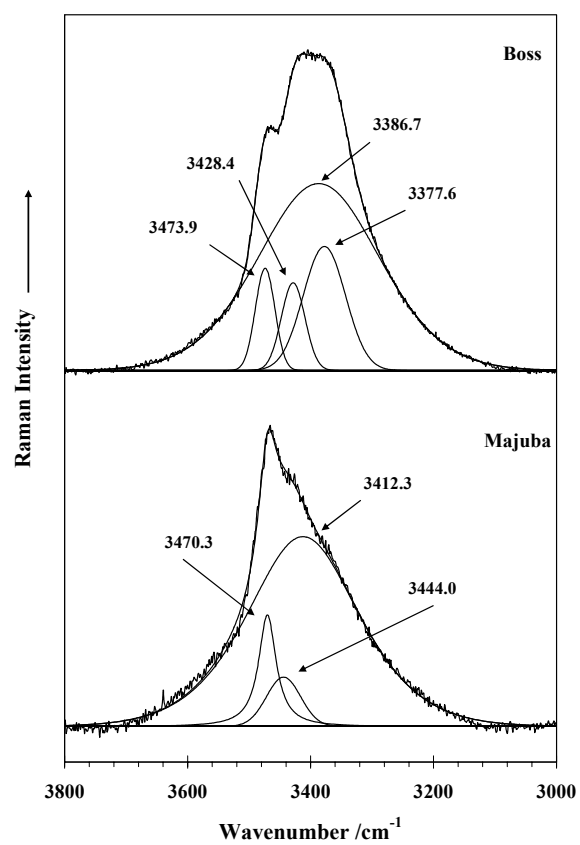


Figure 6